METALLIC LEAD ELECTROREFINING FROM RAW MATERIAL IN LEAD - DIETHYLENETRIAMINE COMPLEX SOLUTION

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ABSTRACT

Metallic lead was refined from raw material via electrolysis process in lead - diethylenetriamine (Pb-DETA) complex solution with presence of various additives. The influence of the additives, Pb-DETA concentration, current density and temperature on lead deposition, dendrite formation and electric current performance were studied. The additives strongly affect to dendrite formation and the deposition of lead metal in the Pb-DETA complex solution. The morphology and composition of the electrolyzed lead were analyzed by optical microscope, scanning electron microscope (SEM) and energy-dispersive X-ray spectroscopy (EDX). After electrorefining, the impurities were removed and the product was pure lead metal. The lead diethylenetriamine complex solution with three additives as gelatine, dextrine and β-naphthol is promising electrolyte for lead refining via electrolysis process.

Keywords: lead, diethylenetriamin, electrorefining, additives.

1. INTRODUCTION

Lead is a familiar metal in our daily life with various applications in electric industry, paint technology and health analysis services. 80 % of this material is used to product lead-acid battery which is still important energy storage system for automobile and electric vehicles [1]. For this application, refined lead metal is required and both of pyrometallurgy and hydrometallurgy processes could be used. However, the best way to refine lead from raw material is electrorefining process because of higher recovery rate of precious metals and lower energy consumption [2]. There are many kinds of electrolyte for lead electrolysis as sulfate, sulfamate, perchlorate, amidosulfonate, hexafluorosilicate, tetrafluoborate, methanesulfonate, and alkaline solutions [1 - 6]. But there are still some problems happen with these electrolysis conditions such as: dendrite formation, chemical consumability and the harmful effects and toxicity of the electrolyte solutions. The complex solution of lead and diethylenetriamine (DETA) was used successfully for lead electrowinning from lead battery paste with high current

efficiency. This solution is promising electrolyte for lead electrorefining because of low harmfulness and toxicity [7].

There are many lead mining areas and estimately 13 milion tons of lead metal reserve in the Northen and Central of Vietnam. However, there is only lead pyromettalurgy process in Vietnam and the product - raw lead metal (98 %) was almostly exported to China. On the other hand, yearly, 10 thousand tons of pure lead metal (99.99 %) were imported for lead-acid battery production. Therefore, the electrolysis for lead metal refining is very important for the stability of the lead - acid battery industry in Vietnam. In this study, lead electrorefining from Yen Bai (Vietnam) raw lead anode in lead/DETA complex electrolyte solution was studied with a variety of additives, current densities and electrolysis temperatures. The dependence of the dendrite formation on the additives was investigated and the suitable electrolysis conditions were optimized.

2. EXPERIMENTAL

The anode electrode was prepared from raw lead metal from a pyrometallurgy factory in Yen Bai, Vietnam and the cathode electrodes for lead electrorefining were prepared from stainless steel. The chemical composition and operating conditions for lead electrolysis are presented in Table 1. All experiments were done during two hours with solution stirring by magnetic bar at 300 rpm. The cathode edges and corners were covered by epoxy resin to protect these parts from the convergence of the electric current which will form lead powdered deposition or surface burning.

Table 1. Solution composition and operating conditions of electrodeposited coating bath.

Chemicals	**Composition**
PbO	70÷150 g/l
DETA	20÷80 g/l
H_2SO_4 (96 %)	22÷50 ml/l
Gelatine	5 g/l
Dextrine	4.0 g/l
β-Naphthol	0.7 g/l
Operating conditions	
D_c, A/dm^2	1÷3
Temperature, ^{o}C	30÷60

All used chemicals were of analytical purity and supplied from China. The amounts of PbO, DETA (diethylenetriamine - $(NH_2CH_2CH_2)_2NH$) and H_2SO_4 which were used to create electrolyte solution with the concentrations of 0.3; 0.4; 0.5; 0.6 and 0.7 M. The structure of the complex of Pb^{2+}, DETA and SO_4^{2-} is shown in Figure 1. The concentration of three additives which were used in this research (gelatine, dextrine and β-Naphthol) was chosen based on the references [3]. The surface morphology and the chemical composition of the electrolyzed Pb layers on cathode was determined by SEM (JMS-6490, Jeol, Japan) with EDX. The composition

of the raw material and product were also determined by ICP analysis after dissolution in nitric acid.

The electric current performance of the electrolysis process was calculated by using a Copper Coulomb Meter - a copper electrolysis bath with electric current efficiency of 100 % which was conjunctively connected with lead electrolysis bath. The cathodic polarization curves of Pb electrode in the Pb-DETA solution were mesured by Autolab PGSTAT 302N (Netherland) using three-electrode system (Pb as working electrode, Pt mesh as counter electrode and Ag/AgCl as reference electrode).

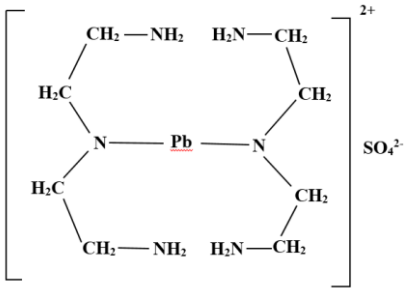

Figure 1. The structure of the complex of Pb^{2+}, DETA and SO_4^{2-}.

3. RESULTS AND DISCUSSIONS

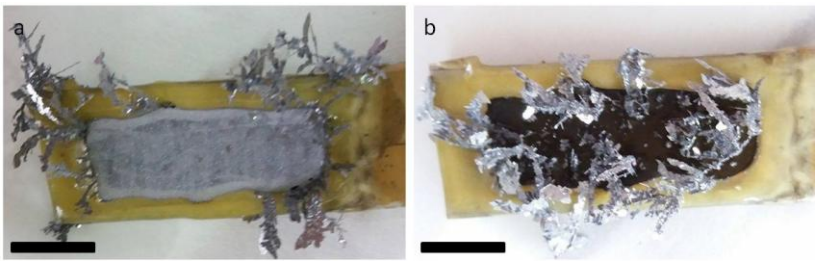

Figure 2. Cathode surfaces after lead electrolysis in the 0.5 M Pb-DETA complex solution without additives after 2 hours at (a) 1 and (b) 3 A/dm^2. Scale bar is 20 mm.

The optical images of the cathode surface after electrolysis in the electrolyte solution without additives are shown in Figure 2. The dendrite formation was apparently happened on the surface of the cathode, especially at the edges of the electrode at low electric current density (1 A/dm^2). Under the higher electrolysis current density (3 A/dm^2) after 2 hours electrolysis, the burning of the electrode surface happened and powdered products were formed. In the actual electrolysis, to increase the working performance of the electrolysis bath, the distance between anode and cathode is minimized and normally smaller than 10 cm. Under the actual electrolysis time is quite long (7÷10 days), the electric accident could happen because of the development of the dendrite to contact to the surface of the anode. Therefore, without additives, the complex solution of Pb and DETA is not accordant to lead electrolysis process.

To determine the optimum Pb electrolysis current density in the Pb-DETA solution, the cathodic polarization curves were mesured and the result is shown in Figure 3. It is clearly that the limit current density increases from 5 A/dm^2 to 5.5 A/dm^2 when the additives are added to

the electrolyte. Therefore, the 1÷3 A/dm^2 was chosen as electrolysis current density of Pb electrolysis in the Pb-DETA solution.

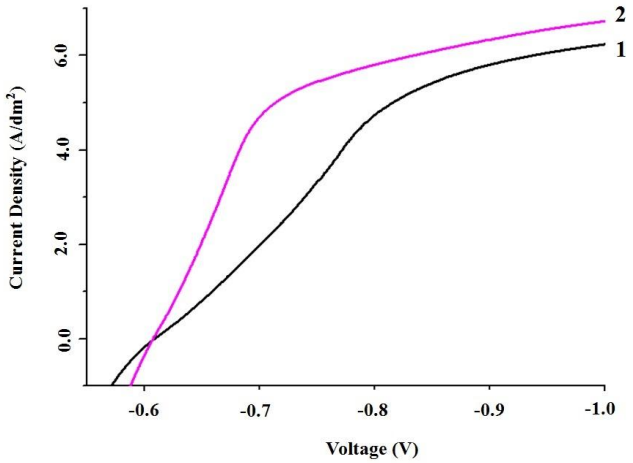

Figure 3. The cathodic polarization curves of Pb electrode in the Pb-DETA solution (1) without additives and (2) with gelatine (5 g/l), dextrine (4 g/l) and β-naphthol (0.7 g/l) additives.

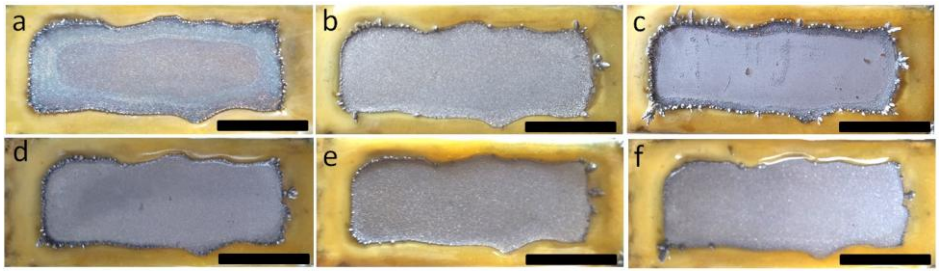

Figure 4. Optical images of the cathode surfaces after 2 hours electrolysis in the lead/DETA complex solutions with different additives as: a) gelatine (5 g/l); b) dextrine (4 g/l); c) β-naphthol (0.7 g/l); d) gelatine (5 g/l) and dextrine (4 g/l); e) gelatine (5 g/l) and β-naphthol (0.7 g/l); f) gelatine (5 g/l), dextrine (4 g/l) and β-naphthol (0.7 g/l). Scale bar is 20 mm.

Figure 4 shows the optical images of the cathode surfaces after 2 hours electrolysis in the lead-DETA complex solution with different additives at electric current density is 2 A/dm^2. It is clearly indicated that while the additives were added to the lead electrolysis solution, the formation and development of the dendrites on the edges of the cathodes were strongly decreased and no any dendrite formation was seen on the surface of the electrodes. The influence of the additives is based on two mechanisms: i) the formation of the complex between additives and metal ions and ii) the adsorption and desorption of the additives on the surface of the cathodes which increase the limit current density and decrease the formation of the dendrite. Under the electrolysis in the solution with different additives, the formation and development of the dendrite is different. The best result - the minimizing of the metallic dendrite formation and development was received while adding simultaneously three additives: gelatine, dextrine and β-naphthol. With this mixed organic compounds, the dendrite has almostly not been seen on the electrode surface.

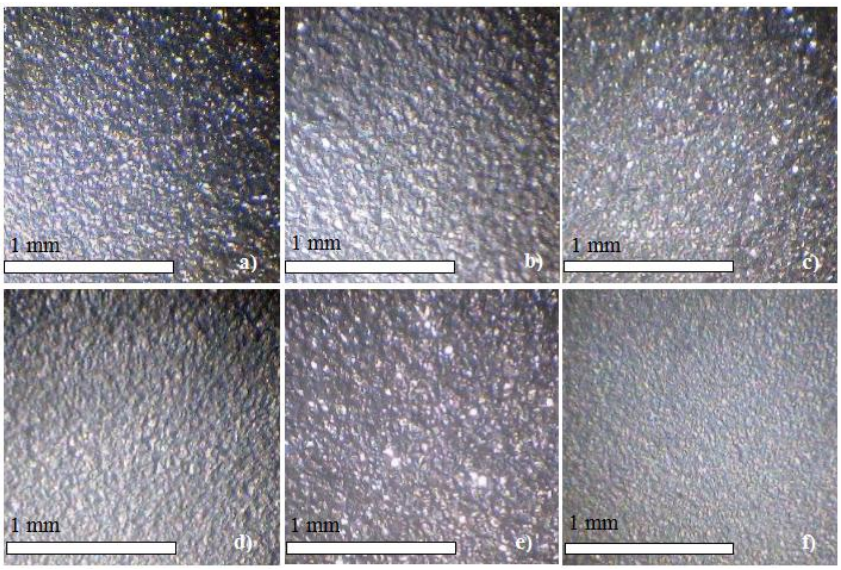

Figure 5. Optical micrographs (40×) of the cathode surfaces after 2 hours electrolysis in the lead/DETA complex solutions with different additives as: a) gelatine (5 g/l); b) dextrine (4 g/l); c) β-Naphthol (0.7 g/l); d) gelatine (5 g/l) and dextrine (4 g/l); e) gelatine (5 g/l) and β-Naphthol (0.7 g/l); f) gelatine (5 g/l), dextrine (4 g/l) and β-Naphthol (0.7 g/l).

After additives were added to the electrolyte solution, not only the dendrite formation was restricted but also the metallic deposite surfaces become brighter and smoother. Especially, the deposited particle size is smaller and more uniformity which can be seen detailly in Figure 5. With the adding simultaneously of three additives: gelatine, dextrine and β-naphthol, the deposited particles are smallest and most uniformity. Therefore, this mixed organic compounds could be used as the additive for the actual metallic lead electrorefining process.

Table 2. Element composition of raw material and electrolized metallic lead determined by ICP analysis.

Elements	Raw material (%)	Electrolized metallic lead (%)
Pb	95.68	99.997
Zn	0.25	0.0006
Fe	1.82	0.0008
Sb	1.45	0.0005
Bi	0.36	0.0004
Sn	0.42	0.0007
Ag	0.01	0
Cu	0.01	0

The surface morphology and the chemical composition of the raw material (anode) and electrolized metallic lead (electrolyzed Pb layers on cathode) which were determined by EDX

and by SEM (JMS-6490, Jeol, Japan) are shown in Figure 6. It is clearly seen that a smooth surface of raw lead anode was created by the pyrometallurgy process where it is difficult to see the grain boundary. While the electrolyzed metallic lead is totally different with big deposited particles and distinct grain boundary. From the EDX analysis, the raw material was determined to contain big amount of ferrous and antimony elements which are harmful impurities for lead acid battery application because of the consequence as the decline in the mechanical properties and the self discharge. After electrolysis, the presence of these impurities was removed. To confirm this result, the element composition of raw material and electrolized metallic lead were determined by ICP analysis which are shown in Table 2. As can be noticed, various impurities such as Fe, Zn, Sb, Bi, Sn, Ag, Cu were determined in the composition of the raw material. After the electrolysis, the deposited metallic lead is almostly pure, the presence of the impurities is minor, so the electrolyzed product could be used for lead acid application.

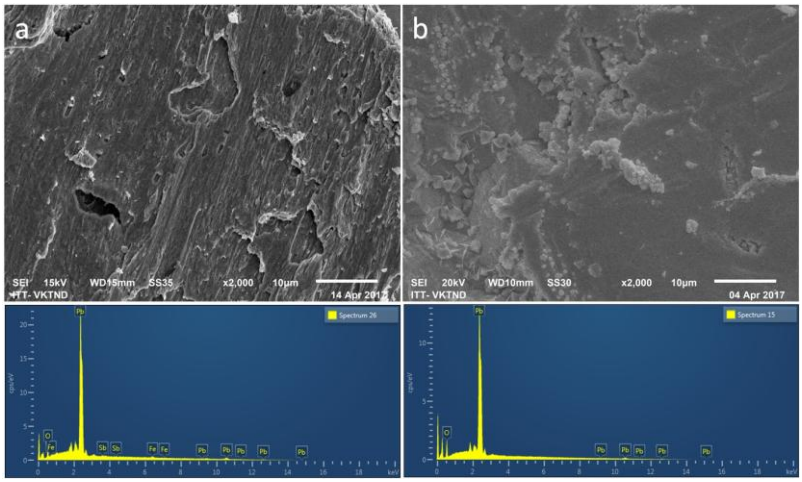

Figure 6. The SEM image of the surface morphology and the EDX analysis of the chemical composition of: a) the raw material (anode) and b) electrolized metallic lead (electrolyzed Pb layers on cathode).

The influence of the electrolysis conditions as electric curent density, lead-DETA complex concentration and temperature on the electric curent performance is shown in Figure 7. At the lead-DETA complex concentration was 0.5 M and the room temperature, the current performance was not significantly modified when the current density changed and the highest performance was approximatly 94 %. However, at the current density was higher than 2.5 A/dm^2, the formation of the dendrite was faster and the burning of the cathode surface was observed. Therefore, the 2 A/dm^2 electric current density on the cathode was chosen for further application.

At the current density of 2 A/dm^2 and room temperature, under the changing of the lead-DETA complex concentration, the current performance increased when the concentration increased from 0.3 M to 0.4 M and then was not significantly modified when the concentration was changed. The highest performance was around 95 % when the complex concentration was 0.5 or 0.6 M. Because of the chemical material saving, the 0.5 M complex concentration was chosen for actual application.

The influence of the electrolysis temperature on the current performance was trivial. Under the electrolysis current density of 2 A/dm^2 and the electrolyte concentration of 0.5 M, the electric current efficiency did not change when the electrolyte solution was modified from 30 ^{o}C

to 60 ^{o}C. The electric current performance was approximately 95 %. For energy saving, the room temperature was chosen as electrolysis temperature for lead electrorefining from raw lead metal in lead-DETA complex solution.

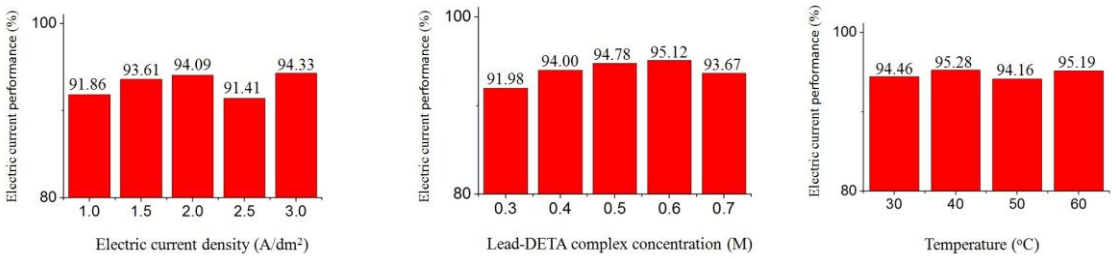

Figure 7. The dependence of electric current efficiency on electrolysis current density, electrolyte concentration and temperature.

4. CONCLUSIONS

Using electrolysis process in lead - diethylenetriamin (Pb-DETA) complex solution, pure metallic lead was produced from raw material. The dendrite formation during lead electrolysis was restricted with presence of three additives as gelatine, dextrine and β-naphthol in the electrolyte solution. The best electrolysis conditions for lead refining in the Pb-DETA complex solution are: i) current density on cathode is 2 A/dm^2, ii) electrolyte concentration is 0.5 M and iii) electrolysis temperature is room temperature. This electrolysis process is promising method for actual metallic lead refining for lead acid battery application.

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